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ON THE ELECTRONIC SPECTRA OF α-FLUORONAPHTHALENE IN THE LIQUID AND SOLID STATES*

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ABSTRACT. The electronic absorption spectra of α-fluoronaphthalene in the liquid and solid states have been analysed and compared with the spectrum of the compound in the vapour state reported by previous workers. The substance in different states is found to exhibit two systems of bands in the 3200—3000 A.U. and 2900—2600 A.U. regions The 0,0 band of the first system shows a shift of 442 cm^{-1} towards red when the vapour is liquefied. When the liquid is solidified and cooled to − 180°C, the 0,0 band is further displaced slightly towards longer wavelengths and the bands become sharper. The second system of bands due to the liquid consists of very broad bands and the 0,0 band is shifted towards red by about 1100 cm^{-1} from its positions in the spectrum due to the vapour. With solidification of the liquid no further change is observed in this system.

INTRODUCTION

Naphthalene and its monoderivatives are known to exhibit two systems of absorption bands in the near ultraviolet region. It was observed in previous investigations (Deb, 1954; Banerjee, 1956) that with change of state and temperature the bands of the two systems due to some monosubstituted naphthalene compounds undergo large changes indicating strong influence of intermolecular forces on the electronic energy state. Such an influence in the case of fluoronaphthalenes had not been studied before The present work was therefore undertaken to study the absorption spectra of α-fluoronaphthalene in the liquid and solid states and to compare the results with those due to the substance in the vapour state.

EXPERIMENTAL

The sample of α-fluoronaphthalene was obtained from Eastman Kodak Co. and was repeatedly distilled under reduced pressure before use. Thin films of the substance of thickness of the order of a few microns yielded the bands in the 2600—2900 A.U. region while much thicker film was required to obtain the bands of the first system on the longer wavelength side. The spectra were photographed on Ilford HP3 films with a Hilger E1 spectrograph. Microphotometric records

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of the spectrograms were taken with a Kipp and Zonen type Moll microphotometer. The wavelengths of the absorption peaks were determined with the help of microphotometric records of iron arc lines photographed on each spectrogram by the method described in an earlier paper (Banerjee, 1956).

RESULTS

The microphotometric records of the spectrograms are reproduced in Figs. 1 and 2 and the frequencies of the bands in cm^{-1} with probable assignments are

TABLE I

Absorption bands of α-fluoronaphthalene

	Vapour* Ramamurty *et al.* (1957)		Liquid at 28°C Present author		Solid at −180°C Present author	
	Wave number (cm^{-1}) and intensity	Assignment	Wave number (cm^{-1}) and intensity	Assignment	Wave number (cm^{-1}) and intensity	Assignment
First system	31872 s	0,0	31430 s	0,0	31348 s	0,0
	32281 m	0+409	32093 mb	0+663	31817 m	0+469
	32545 m	0+673	32500 m	0+1070	32042 s	0+694
	32710 vw	0+838	32866 s	0+1436	32416 m	0+1068
	32918	0+1046	33530 s	0+663+1436	32786 s	0+1438
	33307 m	0+1435			33092 w	0+1068+694
					33474 m	0+1438+694
Second system		(Separation from 0,0)				
	35222	0	34100 wb	0,0	34158 m	0,0
	35399	177	35111 wvb	0+1011	34982 m	0+824
	35683	461	36132 wvb	0+2×1011	34158 m	0+1375
	36053	831			36370 w	0+1375+824
	36341	1119				
	36598	1376				
	36807	1585				
	37075	1853				
	37512	2290				
	38026	2804				
	38481	3259				

*Bands corresponding to fundamental upper state frequencies only have been included.

given in Table I. The spectrum of the compound in the vapour state was studied earlier by Ramamurty *et al.* (1957), whose data have been included in the table for comparison. The compound in all the three states is found to exhibit two systems of bands in the regions 3200--3000Å and 2900—2600Å and these have been designated in this paper as the first and the second system respectively.

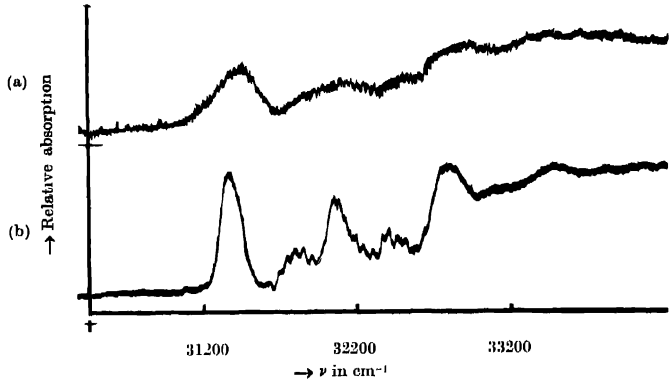

Fig. 1. Microphotometric records of the u. v. absorption spectra of α-fluoronaphthalene (first system).
(a) Liquid at 28°C (b) Solid at — 180°C

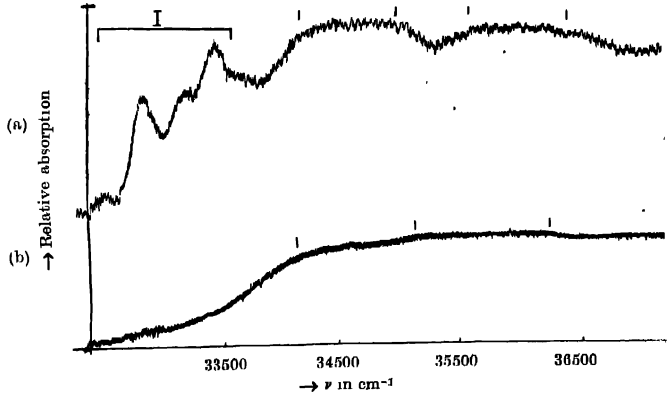

Fig. 2. Microphotometric records of the u. v. absorption spectra of α-fluoronaphthalene (second systeme).
(a) Solid at –180°C (b) Liquid at 28°C
(The bands marked I belong to the 1st system)

DISCUSSION

(*i*) *Bands of the first system* :

The absorption spectrum of α-fluoronaphthalene in the vapour state shows a number of bands with the 0,0 band of this system at 31872 cm^{-1} (Ramamurty, Rao and Rao, 1957), the other band representing excited state vibrational frequencies 409, 673, 838, 1046 and 1435 cm^{-1}. In the spectrum due to the liquid five bands are observed, the first band on the long wavelength side with its centre at 31430 cm^{-1} being assigned as the 0,0 band (Fig. 1). This indicates a shift towards red of 442 cm^{-1} of the 0,0 band with the liquefaction of the vapour. The other bands in the spectrum of the liquid are a little broad and are found to correspond to excited state fundamental frequencies 663, 1070 and 1436 cm^{-1}. Owing to the broadening of the bands, the 409 cm^{-1} band merges with the 673 cm^{-1} band. In the spectrum of the solid at −180°C seven bands are observed, which are sharper than those due to the liquid. The 0,0 band, which is the first and the most intense band of the system on the long wavelength side, is at 31348 cm^{-1}, showing a further shift towards red by 82 cm^{-1} with the solidification of the liquid. In the case of the solid, bands corresponding to the excited state vibrational frequencies 469, 694, 1068 and 1438 cm^{-1} are observed.

The shifts in the position of the 0,0 band with change from vapour to liquid and from liquid to solid state are similar to those observed in the case of α-chloro- and α-bromonaphthalene (Deb, 1954) This indicates that in the case of this molecule also the excited electronic energy level is lowered by the intermolecular field in the condensed phases of the substance in the same way as observed in the spectra of the other two compounds

(*ii*) *Bands of the second system* .

The bands in the spectrum of the liquid in this system are broad and are separated from each other by about 1011 cm^{-1}. The long wavelength edge of the first band is at about 34100 cm^{-1}. In the case of the vapour broad and diffuse bands have been reported by Ramamurty *et al.* (1957). The first band on the long wavelength side at 35222 cm^{-1} has been taken to be the 0,0 band and this band is accompanied by two other bands on the short wavelength side separated from it by 177 and 461 cm^{-1} respectively. Other bands in the spectrum of the vapour are also similarly grouped, the mean separation of 461 cm^{-1} being quite prominent. In the liquid state the coalescence of the bands in each group perhaps produces the broad bands and the long wavelength edge at 34100 cm^{-1} may be taken to be the position of the 0,0 band. Thus, the liquefaction of the vapour results in a large red shift of 1122 cm^{-1} in the position of the 0,0 band. This shows that in the case of this compound the influence of intermolecular field in the liquid state is greater on the second system than on the first. In the spectrum of the solid at −180°C, the bands are still broad and the position of the 0,0 band remains almost unaltered with solidification

Thus the main changes in the spectra of both the systems are found to take place with change from the vapour to the liquid state. This probably indicates formation of strongly associated groups of the molecules in the liquid state due to the presence of highly active fluorine atom in the molecule.

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